Intematix

METAL HYDRIDE CENTER OF EXCELLENCE

DOE Hydrogen Program

# High Throughput Combinatorial Chemistry Development of Complex Hydrides

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Intematix Corporation

*In Association with the DOE/Metal Hydride Center of Excellence*

Project ID #STP17

# Overview

## Project Timeline

- Start date: March 2005
- End date: February 2008
- 100% Percent complete

## Budget

- Total project funding
  - ✓ DOE share: $870K
  - ✓ Contractor share: $218K
- Funding received in FY07: $270K

## Partners

- HRL
- Sandia National Lab

## Barriers

- Slow kinetic reaction (E)
- Thermodynamic stability (J)
- Low reversible storage (P)
- In-situ thin film characterization (Q)

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# Objective

## Overall

- Identify and synthesize novel metal hydride systems using high-throughput combinatorial technique
- Identify catalysts to achieve fast reaction kinetics for metal hydride systems and thus support DOE's 2010 targets for start time (4 s), flow rate (0.02 (g $H_2$/s)/kW) and refill time (3 min)

## 2006

- Validate combinatorial nano-synthesis systems for catalyst discovery
- Screen and identify better catalysts for $MgH_2$ + Si system
- Screen and identify better catalysts for complex $LiBH_4$ + $MgH_2$ dehydrogenation and hydrogenation

## 2007

- Synthesize and characterize novel complex hydride materials in thin films format
- Continue catalyst screening on $LiBH_4$ + $MgH_2$ system based on leads obtained in 2006
- Support other MHCoE partners for thin film deposition

## 2008

- Validate Combinatorial Optical Screening technique for complex hydrides such as $NaAlH_4$ and $LiBH_4$

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# Accomplishments

- Validation of two combinatorial synthesis techniques
- Validation of three high throughput screening techniques
- Validation of Optical Screening for complex and simple hydrides
- Catalyst screened: ~100 metals and alloys
- Found better catalyst for $MgH_2$ + Si dehydrogenation
  - Did not identify any effective rehydrogenation catalyst
  - System down-selected due to lack of rehydrogenation at IMX or other Center Partners
- A few catalyst leads found for $LiH+MgB_2$ system hydrogenation, however, this entry point into the system is not very promising
- Catalyst screening in progress for $LiBH_4$ + $MgH_2$ dehydrogenation
- Proven successful synthesis of thin film materials on both known and novel complex hydride materials [e.g. $LiBH_4$ and $Ca(BH_4)_2$]
- Patents filed: 2
- Intematix accomplished validation of its tools for high-throughput combinatorial catalyst screening ahead of schedule

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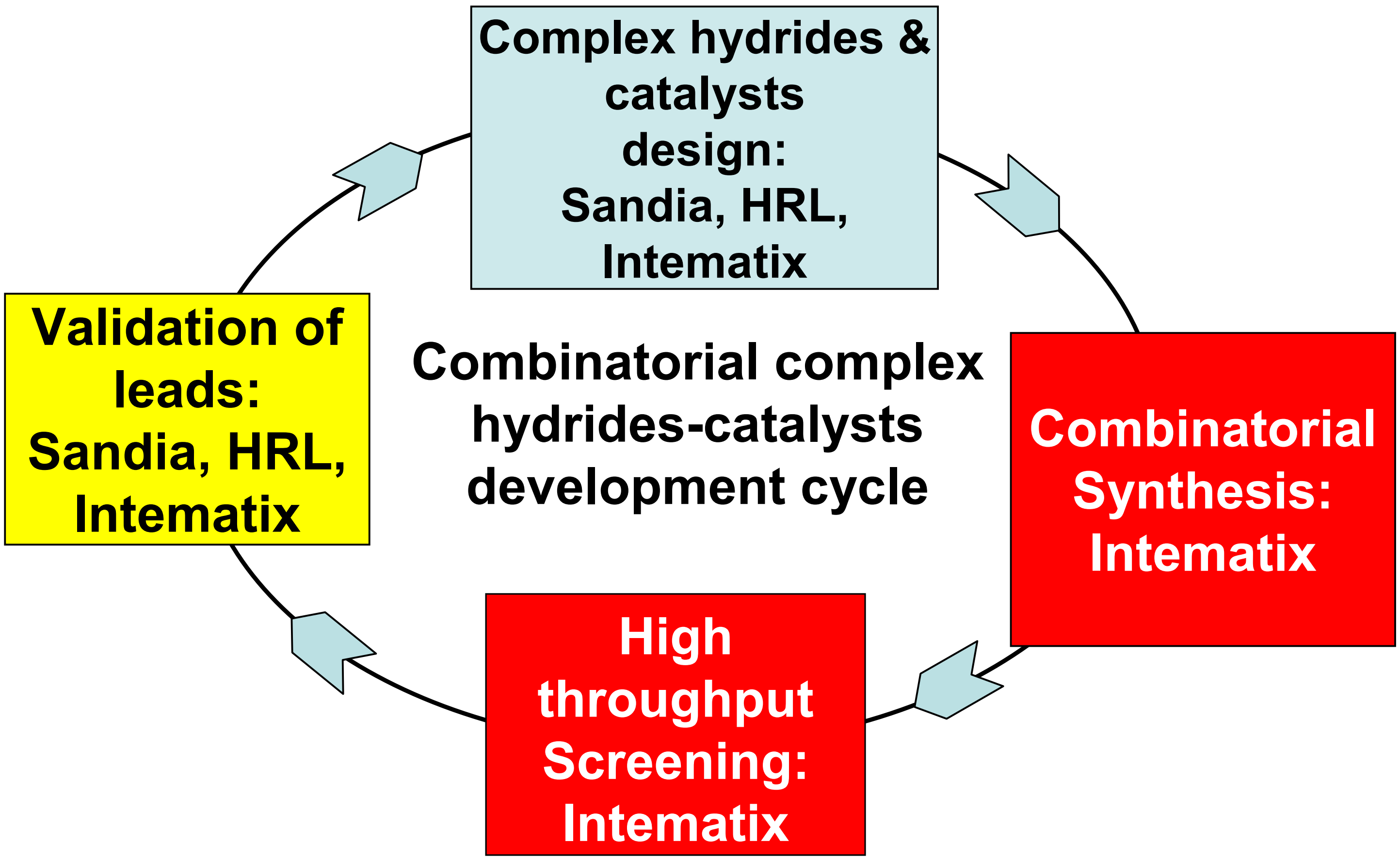
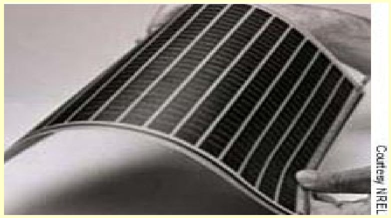
# The Partner Approach

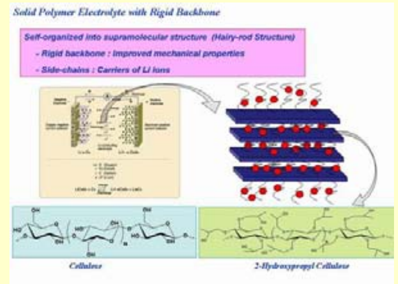
## Methodology used for metal hydride synthesis and combinatorial catalyst screening



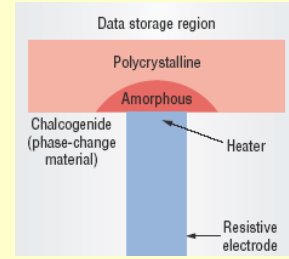
# Intematix's Joint Development Program



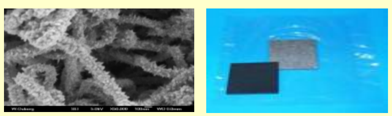

Thin Film Solar Cell & Down Conversion Technology



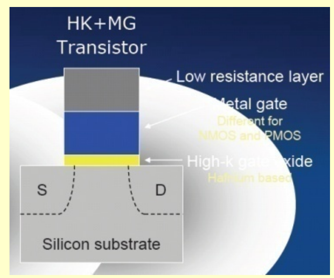

Li Battery Materials



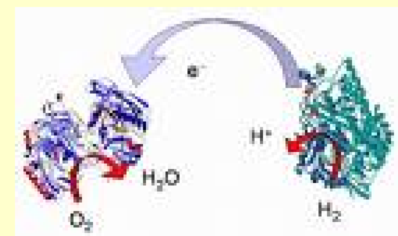

Non-Volatile Memory



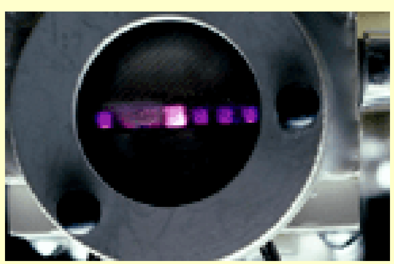
Fuel Cells, $H_2$ Generation and Storage




High-k Metal Gate




Catalysts for Biofuels



Security Phosphor Materials &System

LED, PDP, CCFL Phosphors

# Catalysts Screening for Metal Hydride

**Methodology**

- Combinatorial thin film deposition of catalyst library and in-situ annealing using Ion Beam Sputtering System (primary tool)
- Combinatorial growth of metal nanoparticles using Laser Pyrolysis
- Laser Annealing of metal library in hydrogen pressure cell (Near Future)

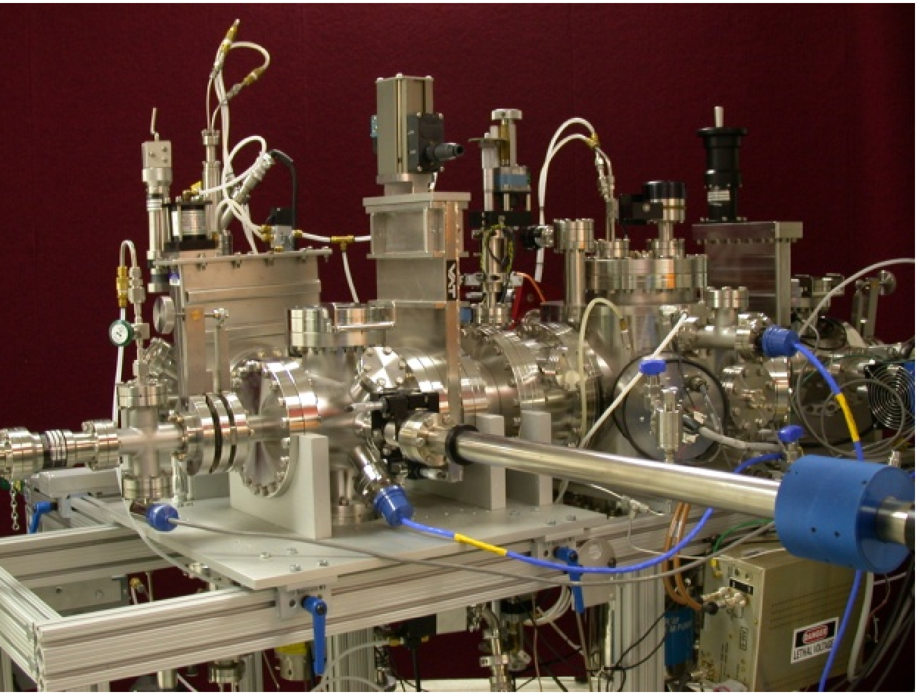
**Techniques**

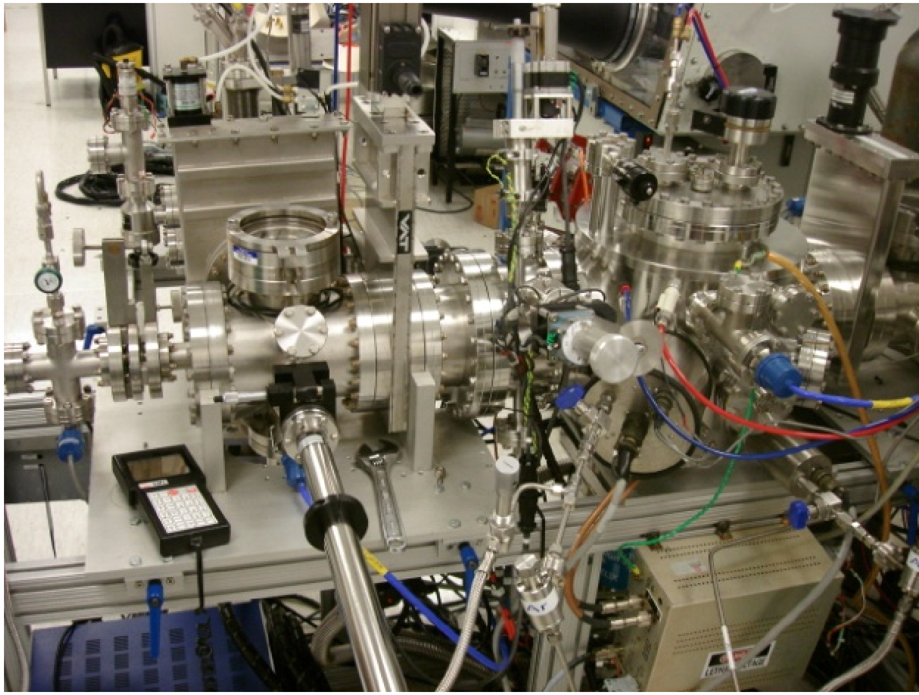
- Real-Time monitoring of optical variations with temperature under different environments
- Optical reflectivity determination (Only for thin film samples)
- Ex-situ scanning X-ray diffraction

**Confirmation**

MHCoE partners collaboration (HRL, SNL)

# Ion Beam Sputtering: A Combinatorial Approach





| | |
|---|---|
| **Advantages** | **Ultra-fast combinatorial materials synthesis** |
| **Capabilities** | **Combinatorial synthesis of metal hydrides and/or catalysts thin films** |
| **Status** | **Validated for metal hydride and catalyst synthesis** |

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# Experimental Details – Catalyst Screening

Catalysts deposition by CIBS on metal hydride on substrates

Transfer to the reactor with optical window

Variations in optical properties recorded versus temperature

For hydrogenation, catalyst library was first screened under Ar and then $H_2$

Results determined by image processing; compared to any existing data*

Confirm the formation of product by XRD
$NaH + Al$ / $NaAlH_4$
$Mg_2Si$ / $MgH_2 + Si$

Methodology for catalyst screening validated by 'rediscovery' of known catalyst as well as discovery of a new, better catalyst.

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# High Throughput Screening Tools-1

## Optical Screening

1) Using High Pressure Optical Chamber
2) Max. Pressure: 600 psi
3) Max. Temperature: 350 ºC
4) Max. Sample Size: 3 x 3 cm

Mg thin film (250 nm) before hydrogenation

$MgH_2$ thin film after hydrogenation

Methodology:

**At constant pressure:**
Change in optical properties versus temperature

**At constant temperature:**
Observe the of change in optical properties versus pressure

Conclusion:

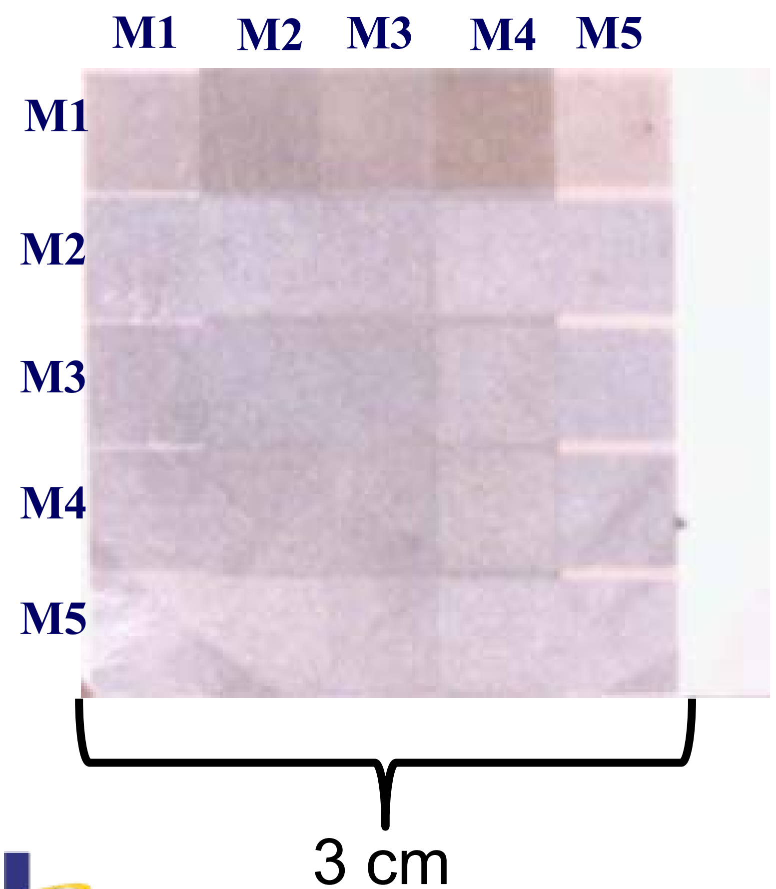
A change in color, as indicated by image processing, at a particular catalyst, indicates that a reaction may have taken place (lead generated for further catalysis study)

Change in optical property is a combination of change in reflectivity and the respective transmission stemming from change in underlying band structure.

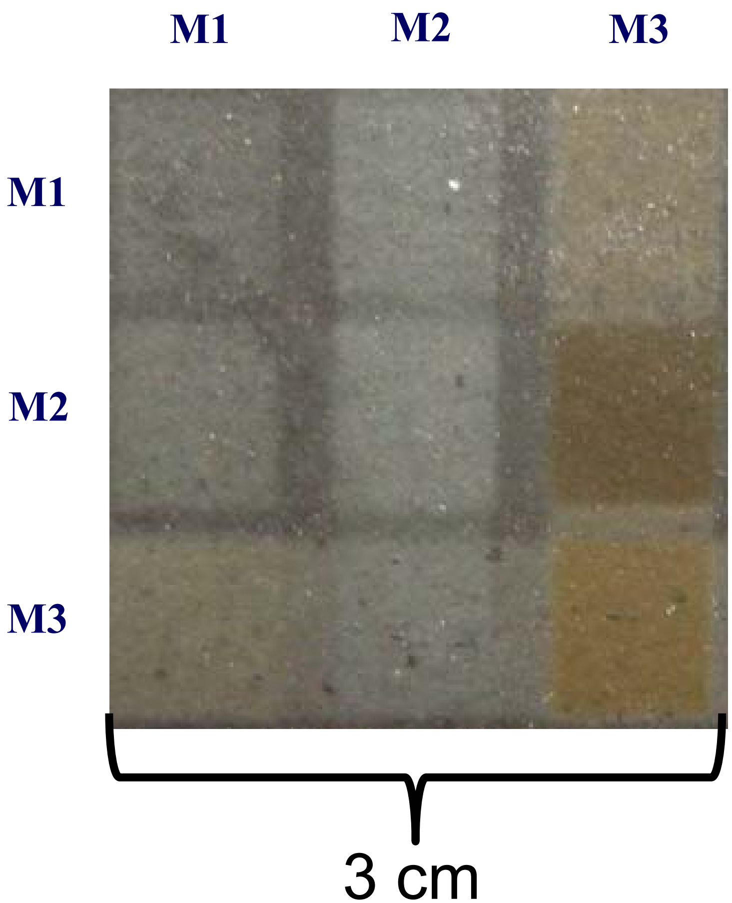
Griessen & coworkers, Scripta Materialia 56, 853 (2007)

# Example Libraries

## Library 1




## Library 2

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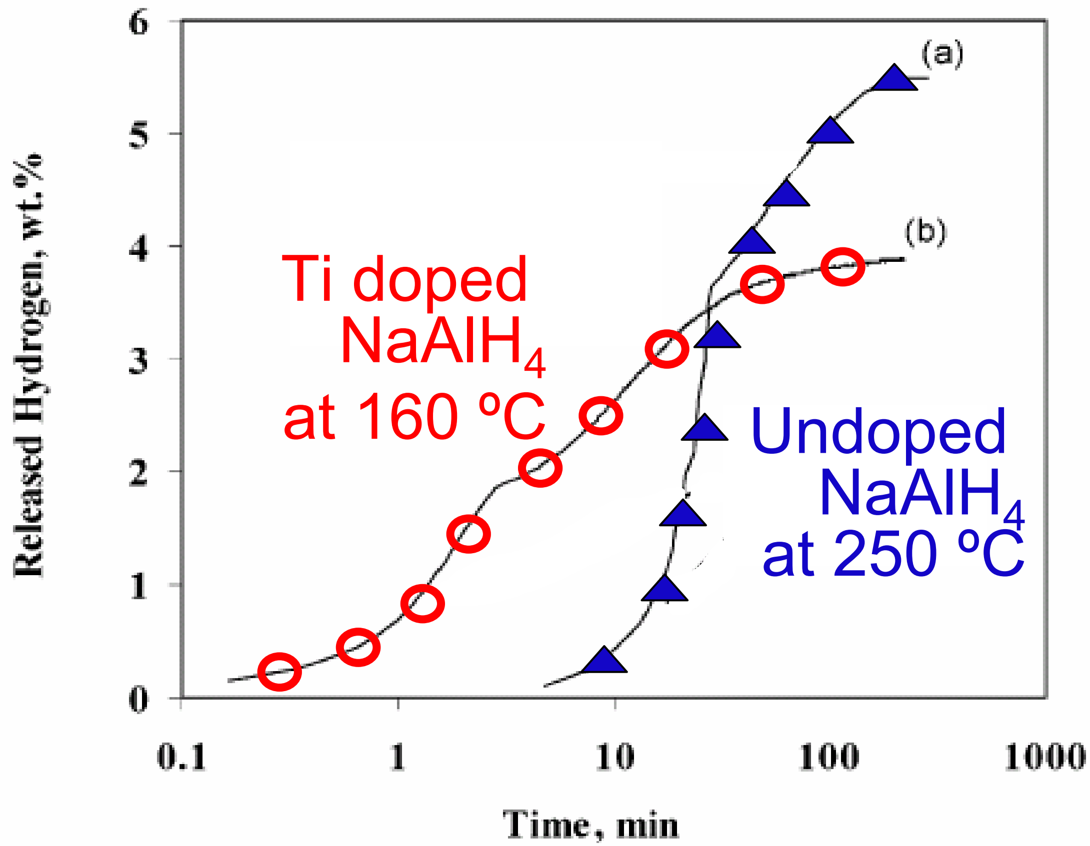
# $NaAlH_4$ Literature




Ti known to catalyze $H_2$ release from $NaAlH_4$

Jensen & coworkers, J. Phys. Chem. B 107, 10176 (2003)

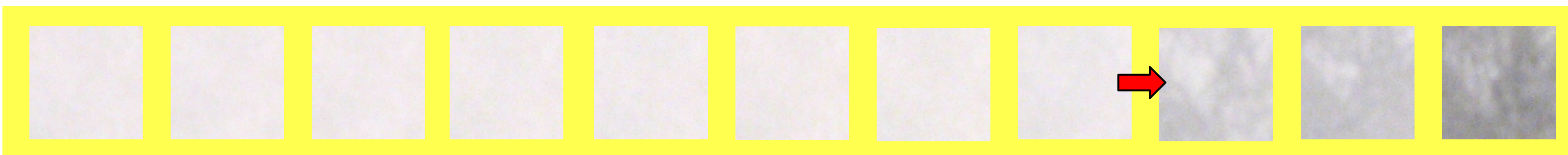
# Validation of Method with $NaAlH_4$

## Experimental Conditions

Gas Environment: Vacuum    Temperature: RT to 200 ºC    Rate: 3 ºC/min

| Temp (ºC) | 25 | 50 | 75 | 100 | 125 | 150 | 175 | 185 | 185 5 min | 200 | 200 90 min |
|---|---|---|---|---|---|---|---|---|---|---|---|

$NaAlH_4$ As available

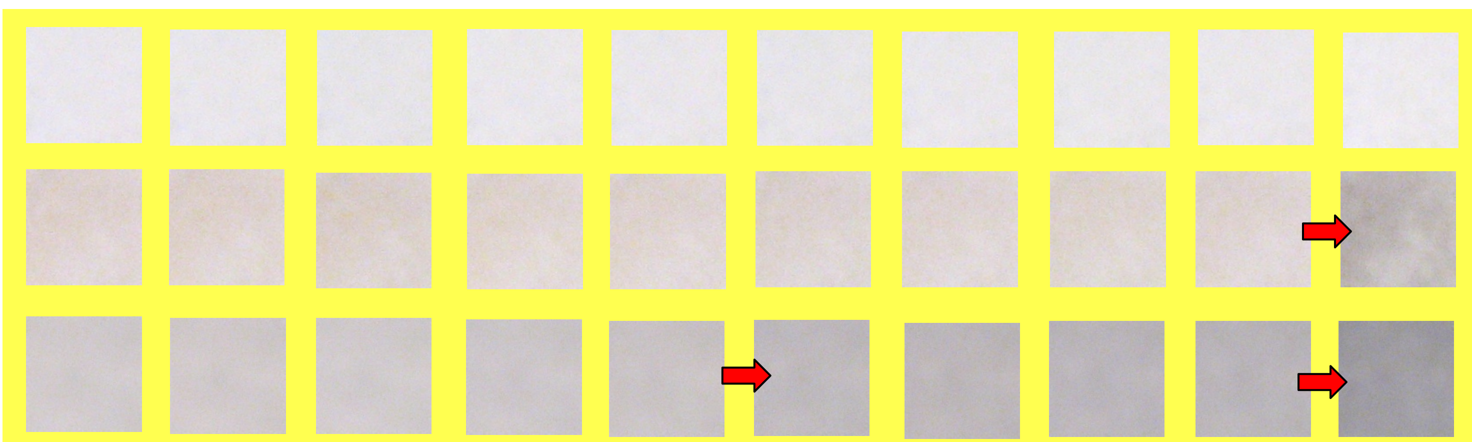


| Temp (ºC) | 25 | 50 | 75 | 100 | 125 | 130 | 140 | 150 | 160 | 160 (30 mins) |
|---|---|---|---|---|---|---|---|---|---|---|

No Ti

100Å Ti film

5% $TiBr_4$*



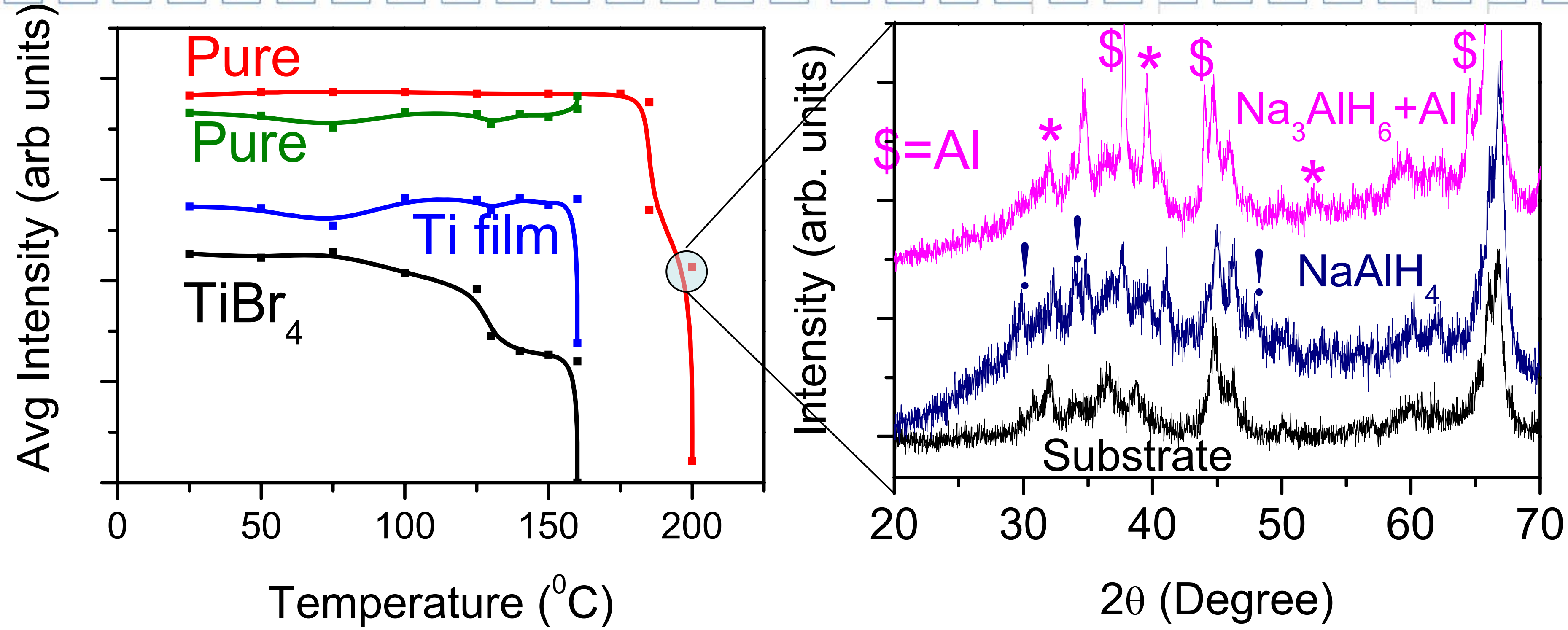
No change

$H_2$ release at 160 ºC

$H_2$ release at 160 ºC

$NaAlH_4$ deposited on the substrate as a slurry in hexane or anhydrous toluene

# Intematix Results: Image Processing and XRD



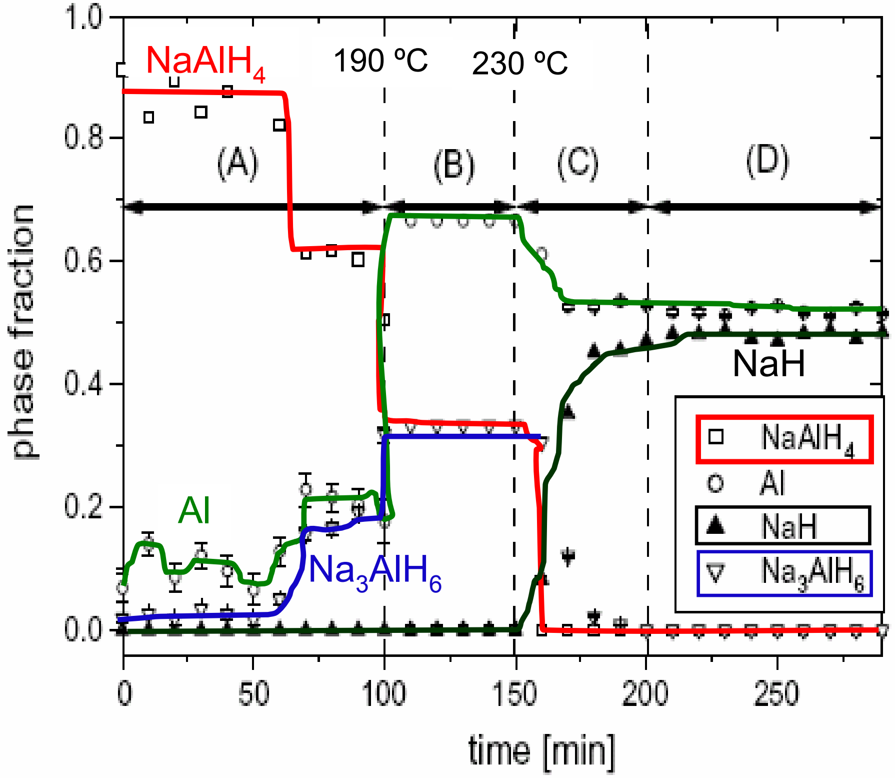

Ti identified as a catalyst for the system

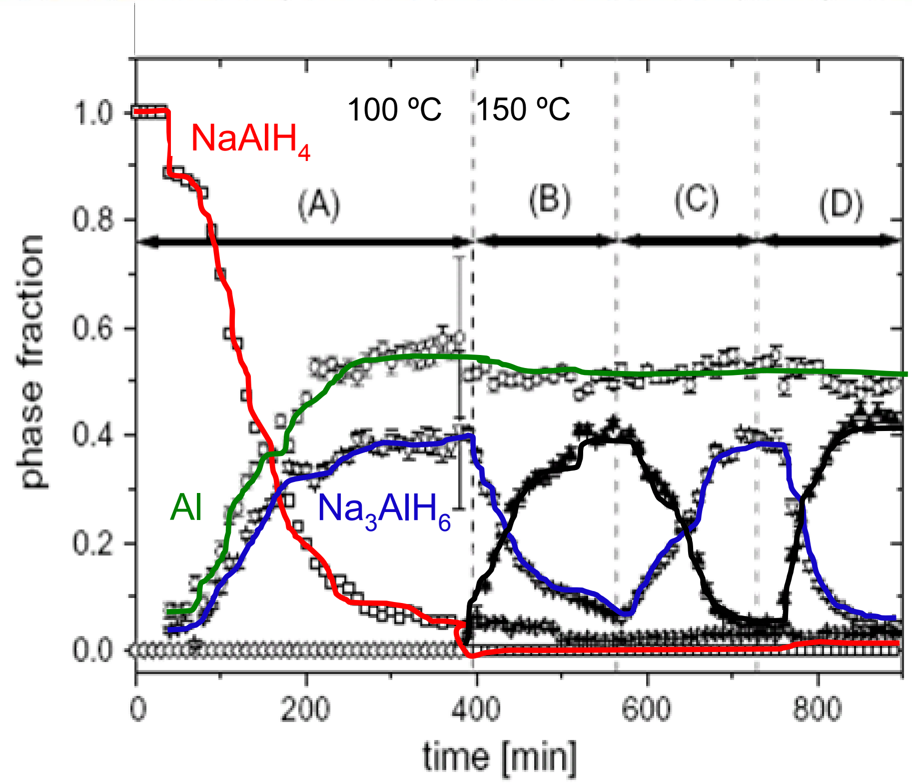
XRD confirms phase change and hydrogen release:

$3NaAlH_4 \rightarrow Na_3AlH_6 + 2Al + 3H_2$

Rehydrogenation attempted but unsuccessful as 500 psi $H_2$ is below the 1500 psi where facile reaction would be expected

# $NaAlH_4$ Literature Matches Experimental Results




Pure $NaAlH_4$ transforms to $Na_3AlH_6$ ~190 ºC

Ti catalyzed $NaAlH_4$ transforms ~150 ºC

Singh et al., Acta Materialia **55**, 5549 (2007)



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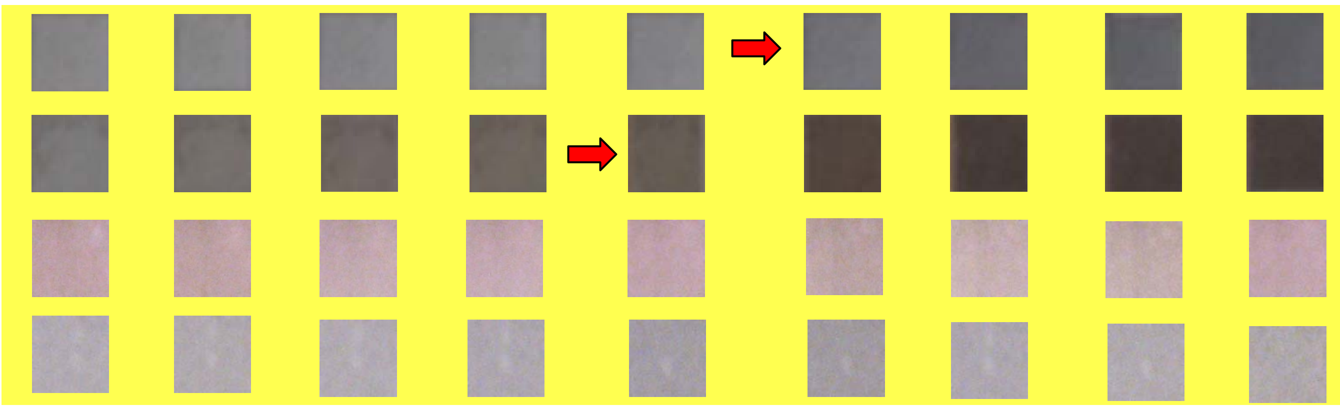
# Validation

- Methodology validated on $NaAlH_4$ system; results both with and without Ti match expected behavior
- Observation of catalysis in “bulk-like” sample
- Observation of catalysis by thin film deposited catalyst sample on a complex hydride
- XRD can be used as direct confirmation of product formation
- These results enable us to trust both the thin film catalyst deposition approach and the sample preparation methodology

# Dehydrogenation – Catalyst Screening for $MgH_2$ + ½ Si Powder

Optical Properties Screening (heated at 3 ºC/min):

(ºC) 25 140 180 190 210 260 300 320 350



| | |
|---|---|
| Ni | $H_2$ release at 260 °C |
| Mn | $H_2$ release at 210 °C |
| Cu | No change observed |
| Fe | No change observed |

- Catalytic effect observed with thin film metal deposited on covalent metal hydride
- Ni known by HRL, Mn previously unknown
- Non-reaction with Cu and Fe thin films confirms catalytic versus morphological nature of thin film Mn and Ni
- We have confirmed that there is no change in the optical properties of pure material under the similar conditions (1 bar Ar, time= 2 hrs, max T = 350 °C)

**Catalysts screened: Ni, Mn, Cr, Fe, Ti, Nb, Pt, V, Cu, and 40 binary alloys**

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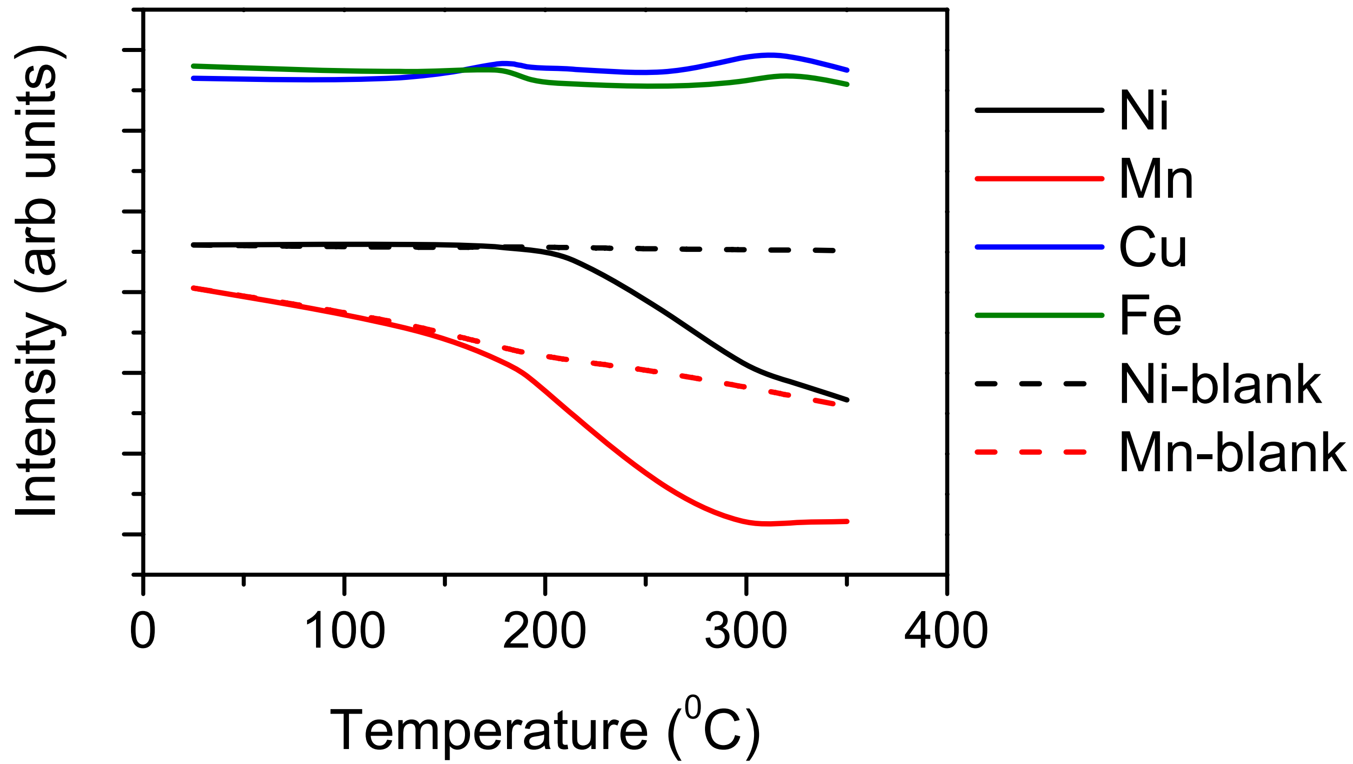
# Image Processing of $MgH_2$ + Si optical screening




- Blanks show effect of heating catalyst in presence of argon
- No difference between blank and experiment for Ni or Mn
- Image processing quantitatively shows transition temperatures, which are key to interpreting results

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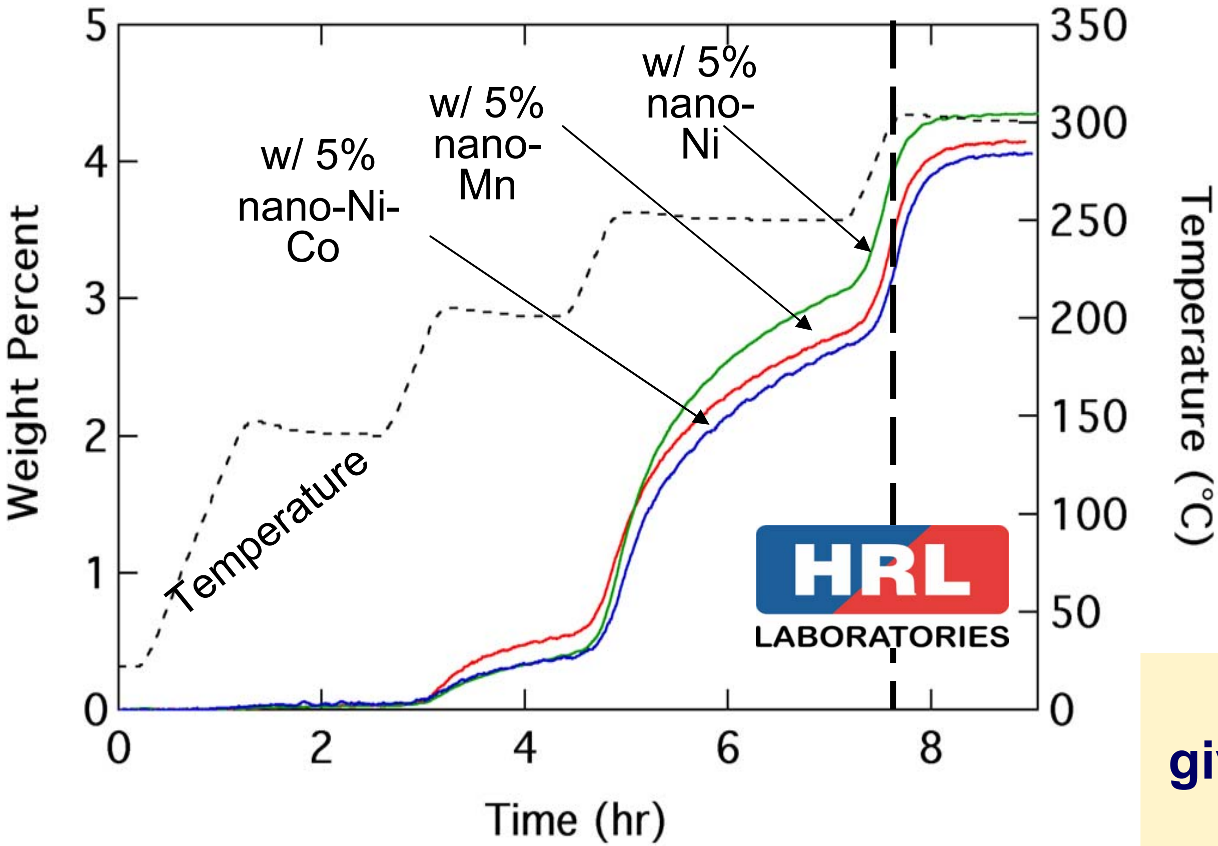
# Hydrogen Desorption Catalyst Confirmation from Center Partner

## $MgH_2$/Si + Catalyst




- A similar approach was used by HRL: heating at 2 ºC/min
- Pure $MgH_2$ + Si takes 7.5 hr for onset of decomposition (shown by vertical dashed line)

**Nano-Mn, Ni and Ni-Co give similar enhancements for dehydrogenation**

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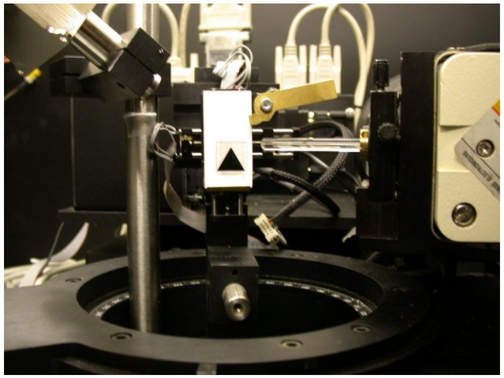
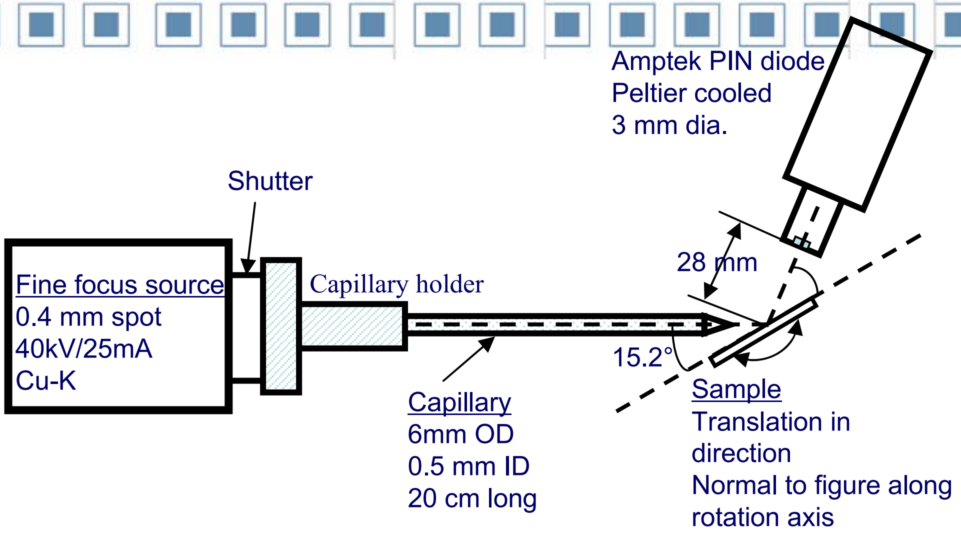
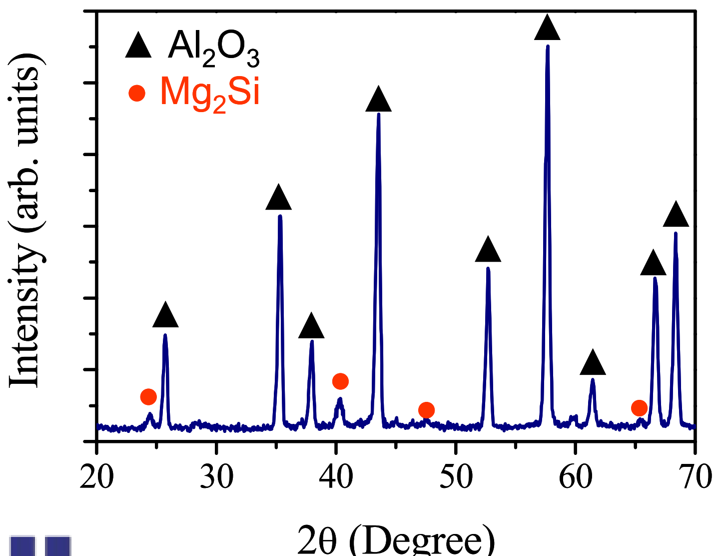
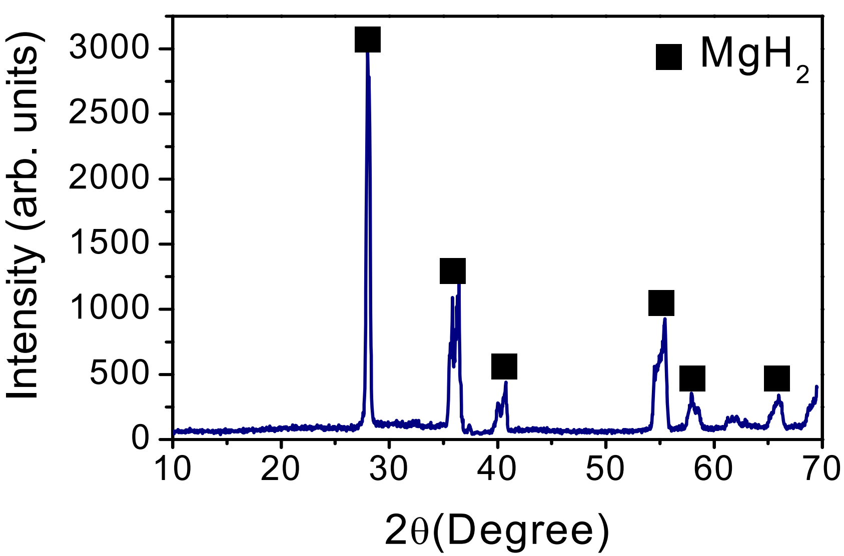
# Micro-beam scanning XRD results






**Limitation:** *Not configured for highly air sensitive materials*



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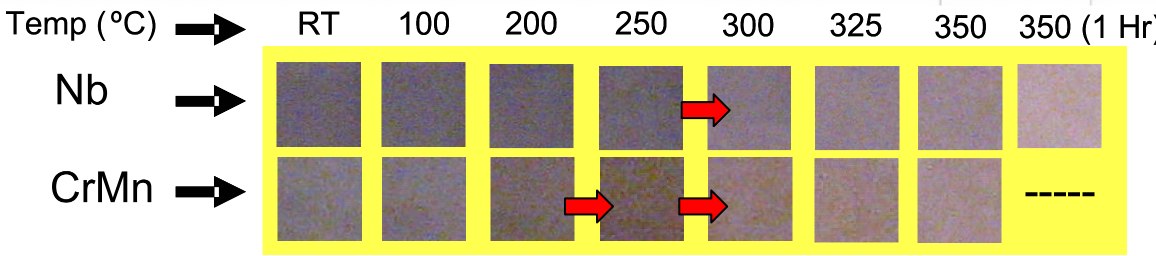
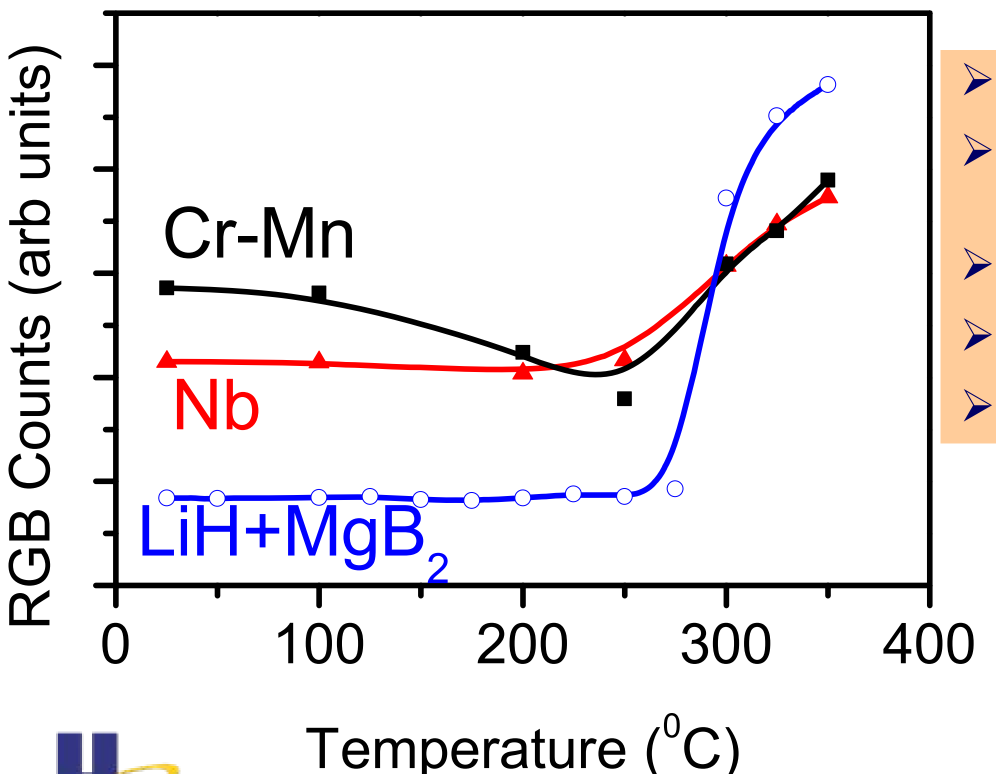
# Hydrogenation – Catalyst Screening for $LiH + MgB_2$




- Evidence for Nb metal, CrMn alloy catalysis
- Screened ~50 catalysts combinations of Fe, Ni, Nb, Pt, Ru, Cr, Mn, Mg, V
- More careful analysis is required
- Most promising results shown here
- Further validation necessary

Also, screened 25 catalyst for Dehydrogenation of $LiBH_4 + MgH_2$

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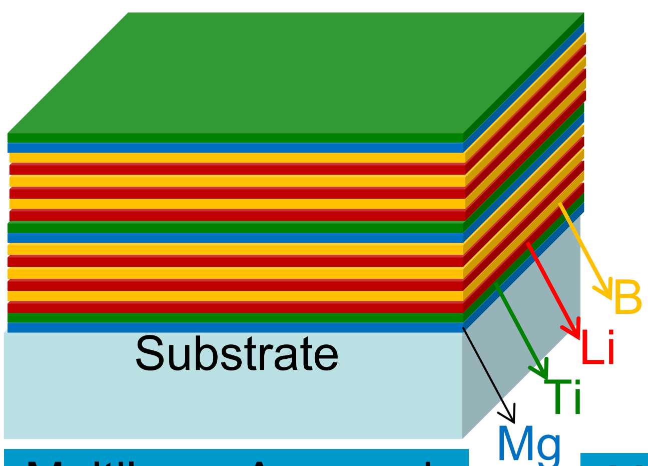
# Thin film systems

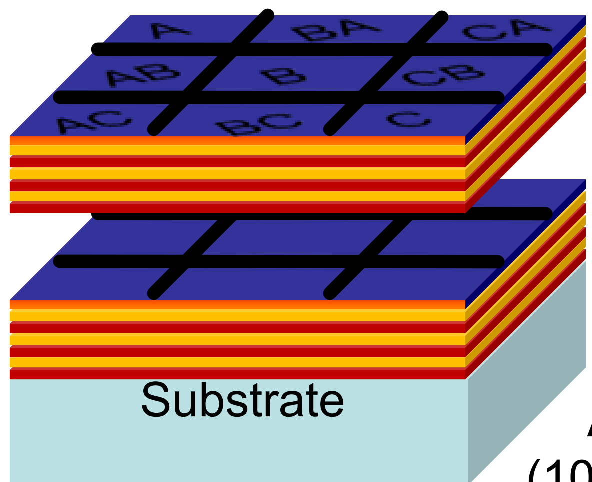
# Combinatorial Thin Film Design Approach

Rationale:

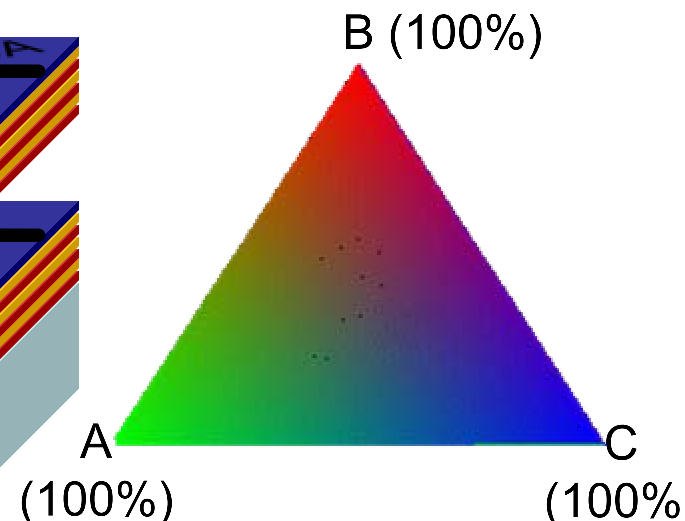
1)Addresses/solves non-uniformity of powdered (ball-milled) sample
2)Opportunity to explore novel nano-material system in a **"controlled"** fashion.
3)Catalysts can be sandwiched between the complex hydride layers increasing effective loading
4)More accurate data accumulation using automated optical reflectivity setup for hydrogenated and dehydrogenated samples.
5)Role of morphology, microstructure and stress on hydrogen storage can be studied effectively
6)Sensitive elements, such as Li, can be deposited very efficiently and effectively.
7)Sample size can be varied depending on the experiments




Multilayer Approach

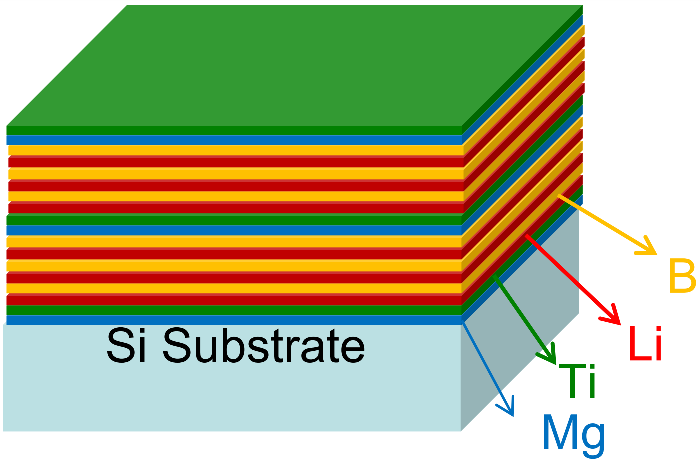



Multilayer + Discrete library

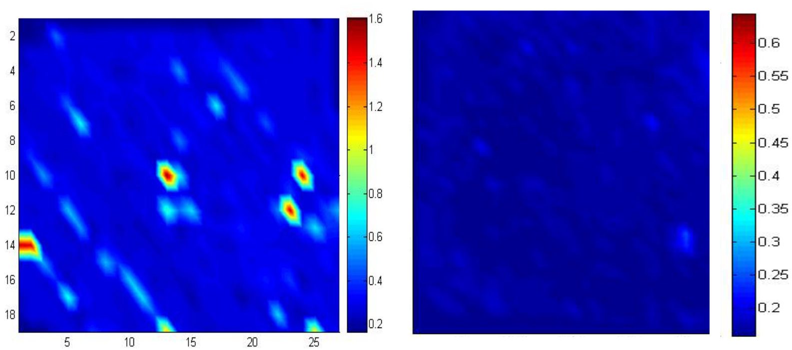


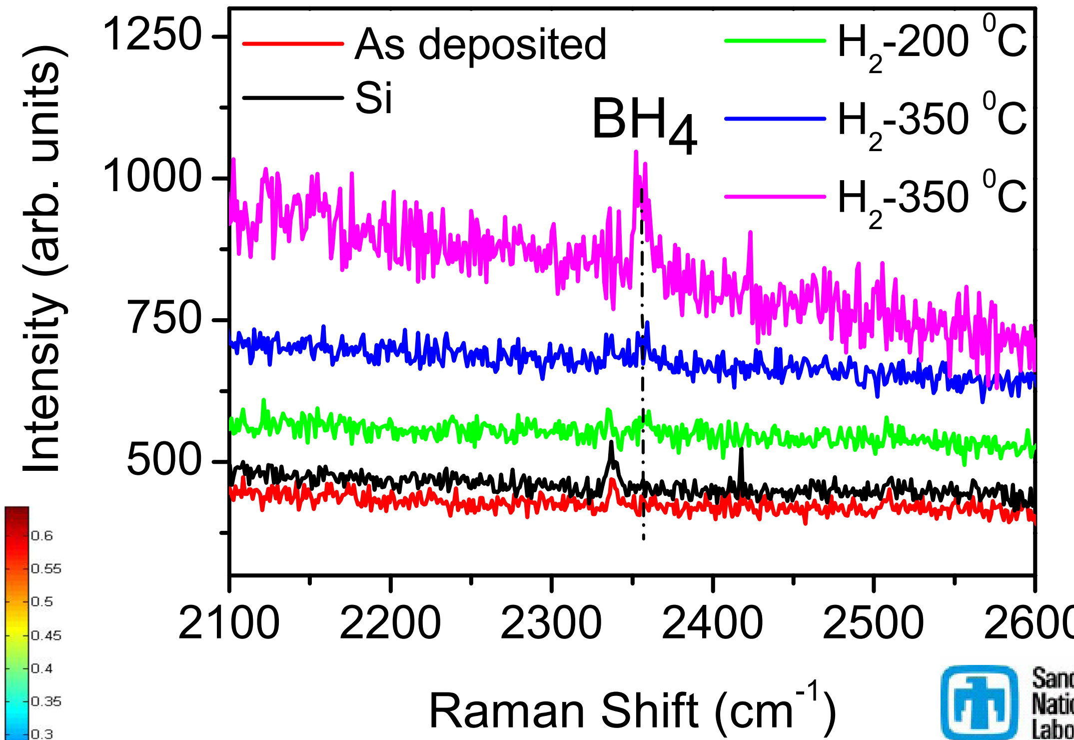

Ternary Continuous library

# Li-B-Mg-Ti Thin Film, 350 ºC and 500 psi $H_2$




(Li=10 Å, B=10 Å) x 5 =100 Å; (Ti=10Å, Mg=10Å) x 1;






False color reflectivity mapping indicates hydrogen uptake (darkening from right to left); confirmed by Raman

Mg & Ti were added as catalysts based on $LiBH_4$ bulk systems in the literature


Vajo et al., J. Phys. Chem. B **109**, 3719 (2005)
Yu et al., Chem. Comm. 3906 (2006)
Au et al., J. Phys. Chem. B **110**, 26482 (2006)

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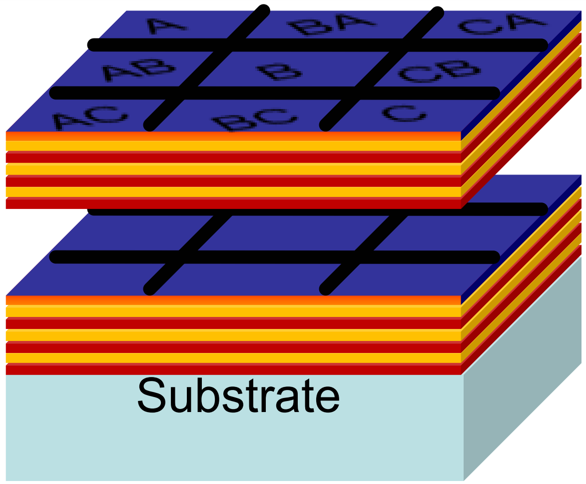
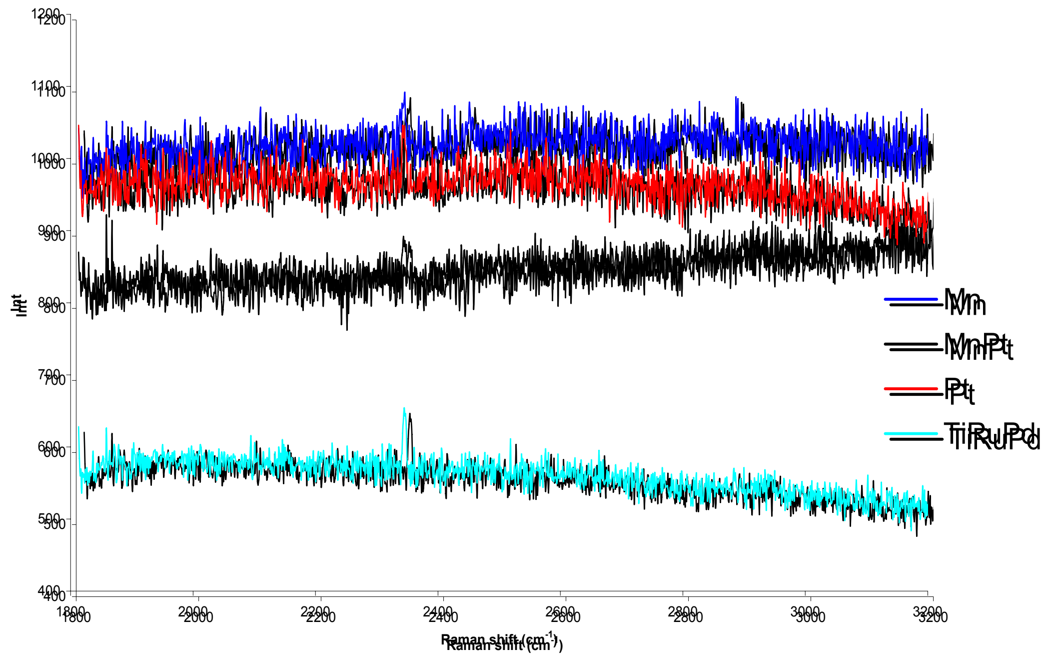
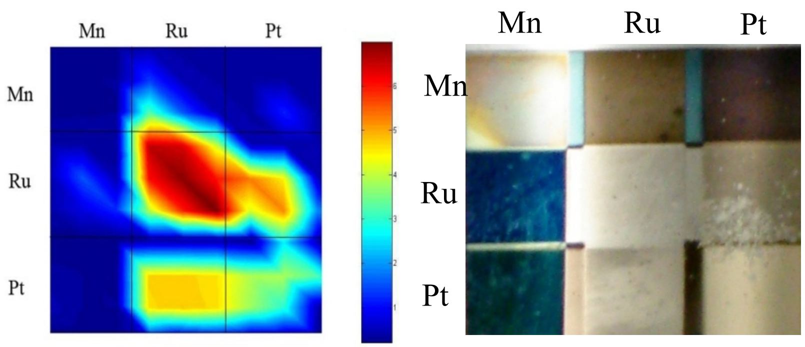
# Ca-B Mixture Thin Film With Catalyst Library




Hydrogenation temperature=440 °C
Hydrogen pressure=15,000 psi




Optical reflectivity and an image of Ca, B mixture with discrete catalyst libraries.

Indication of B-H bond formation, but not necessarily $BH_4^-$, possibly a higher order $B_xH_y^{n-}$, based on the Raman spectra. Such a compound is likely an intermediate in the formation of $BH_4^-$ from elemental B and $H_2$.

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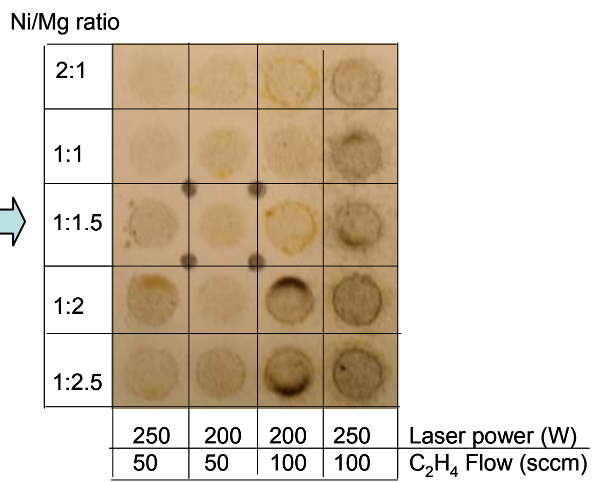
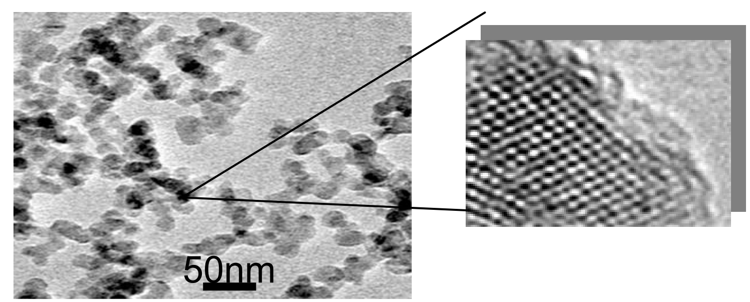
# Complementary Synthesis Technique – Combinatorial Nano-particle (CNP) System

## Capabilities:

- Synthesis of nanoparticles of metals, oxides, hydrides, nitrides, carbides, sulfides, etc.
- Reproducible high crystalline quality nanoparticles with narrow size distribution (< ±30%)
- Synthesis of combinatorial nano-particle libraries with controllable parameters:
  - particle size
  - material composition
  - synthesis conditions
- System has been validated for bimetal alloy libraries

*Typical Example*




For example, this system has generated Ni particles for $Mg_2Si$

# Summary

***Goal:***

Identify catalysts which improve the kinetics and selectivity for desired metal hydride systems to enable an on-board hydrogen storage system which meets DOE 2010 targets.

***Approach:***

Combinatorial nano-catalyst synthesis and high throughput screening to speed up catalyst discovery.

***Technical Accomplishment and Results:***

(1) Improvement in design, setup and validation of combinatorial nano-catalyst synthesis and high throughput catalyst screening processes.

(2) Validation of Optical Screening for complex and simple hydrides

(3) Proven successful synthesis of thin film materials on both known and novel complex hydride materials [e.g. $LiBH_4$ and $Ca(BH_4)_2$]

(4) Ni and Mn were found to be the most effective catalyst for $MgH_2$ + Si system for dehydrogenation. But, NO Reversibility. So, NO-GO system.

(5) Identified a few alloy leads which appear to improve kinetics of LiH + $MgB_2$ system. But more catalyst screening is necessary for further improvement.

***Proposed Future Research:***

Project Complete